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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification<sup>5</sup> :

C08F 6/00, C08L 33/26  
C12N 9/80, C12S 13/00

A1

(11) International Publication Number:

WO 92/05205

(43) International Publication Date:

2 April 1992 (02.04.92)

(21) International Application Number: PCT/GB91/01583

(22) International Filing Date: 16 September 1991 (16.09.91)

(30) Priority data:  
9020081.7

14 September 1990 (14.09.90) GB

(71) Applicant *(for all designated States except US)*: ALLIED  
COLLOIDS LIMITED [GB/GB]; P.O. Box 38, Low  
Moor, Bradford, West Yorkshire BD12 0JZ (GB).

(72) Inventor; and

(75) Inventor/Applicant *(for US only)*: FARRAR, David [GB/  
GB]; 2 Pennyhill Drive, Clayton, Bradford, West York-  
shire BD14 6NH (GB).

(74) Agent: LAWRENCE, Peter, Robin, Broughton: Gill Jen-  
nings & Every, 53 to 64 Chancery Lane, London WC2A  
1HN (GB).

(81) Designated States: AT (European patent), BE (European  
patent), CA, CH (European patent), DE (European pa-  
tent), DK (European patent), ES (European patent), FR  
(European patent), GB (European patent), GR (Euro-  
pean patent), IT (European patent), JP, LU (European  
patent), NL (European patent), SE (European patent),  
US.

Published

*With international search report.*

(54) Title: POLYMERISATION PROCESSES

(57) Abstract

Polymers of (meth) acrylamide are made by exothermic polymerisation of an aqueous polymerisable mixture containing (meth) acrylamide in a reaction vessel and recovering the polymer from the reaction vessel, generally in particulate form, and the residual (meth) acrylamide content of the polymer is reduced by incorporating amidase in the polymerisable mixture.

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## Polymerisation Processes

This invention relates to the production of polymers of (meth) acrylamide in a manner such that the polymers have remarkably low levels of contamination with monomeric (meth) acrylamide.

5        Polymers of (meth) acrylamide are made by providing a polymerisable mixture containing the (meth) acrylamide and polymerising the polymerisable mixture. Usually the process is conducted in a reaction vessel and the resultant polymer is recovered from the reaction vessel. Often it is in particulate form, either as a dispersion in liquid or as a dry powder. However in some instances the polymerisable mixture is polymerised at the intended place of use, for instance after injection into soil to form a soil stabilising polymer.

15        Even when the polymerising conditions in a reaction vessel are subject to careful control, it is normal for the polymeric product to be contaminated with a small amount of residual (meth) acrylamide. It is known to reduce this contamination by chemical treatment of the preformed polymer, for instance by the addition of bisulphite. However this chemical post-treatment necessitates an additional processing step and can have undesirable effects on the properties of the preformed polymer.

20        It is also known to reduce the (meth) acrylamide contamination of preformed polymer by adding an amidase to the polymer and thereby treating the polymer with the amidase so as to reduce the amount of free (meth) acrylamide in the polymer. Such processes are described in U.S. 4,687,807 and in EP 0329324 and 0329325. These processes again have the disadvantage that they require an extra process step. Another problem is that amidase are generally regarded as being heat sensitive with the result that conventional thinking dictates that the processing conditions should avoid exposing the amidase to elevated temperatures.

Conventional considerations therefore lead inevitably to the desirability of minimising residual (meth) acrylamide primarily by careful control of the polymerisation conditions, for instance by selection of the amount of initiator and the rate of initiator addition, and by these techniques it is possible in commercial practice regularly to obtain residual (meth) acrylamide contents of well below 2%, for instance below 1% and often below 0.5%.

Since monomer contamination can be a significant problem even when the polymerisation is carried out under carefully controlled conditions in a reaction vessel, it is not surprising that significant amounts of monomer residues are liable to occur under the relatively uncontrolled conditions that prevail when the polymerisation mixture is, for instance, injected into a subterranean location for soil stabilisation, grouting, shut-off or similar purposes. Under these circumstances the amount of monomer contamination can be high (several percent).

The polymerisation conditions that prevail in an injected soil stabilisation or similar mixture are not capable of being controlled accurately but they do have one advantage, which is that the polymerisation temperature is usually low, for instance 40°C or less, since the soil or other material into which the mixture is injected acts as a heat sink and keeps the process cool.

It has been proposed in, for instance, JP-A-55/135191 and JP-B-61/39356 to include amidase in the injected polymerisation mixture to reduce the amount of residual acrylamide.

Because of the relatively high residual monomer contamination in the absence of amidase any reduction in residual monomer by the amidase addition would be very beneficial even if the final level is still quite high. Some deactivation of the amidase would be tolerable simply because, even after deactivation, the amidase could be expected to reduce monomer contamination usefully below the rather high values that would otherwise be present. Also,

since the processes are relatively cool (below 40°C or less) it would be expected that the amount of temperature deactivation would be low.

5 The proposal to use amidase to reduce the amount of residual monomer in a low temperature process that gives relatively high residual monomer amounts is therefore of no relevance to someone concerned with the much more sensitive problem of reducing the already low contamination (e.g., below 0.5%) in a highly exothermic polymerisation conducted  
10 in a factory.

A process according to the invention for making a polymer of (meth) acrylamide comprises providing an aqueous polymerisable mixture containing (meth) acrylamide in a reaction vessel, exothermically polymerising the  
15 polymerisable mixture and recovering the resultant polymer from the reaction vessel, and in this process the residual (meth) acrylamide content of the polymer is reduced by incorporating amidase in the polymerisable mixture.

The polymerisation proceeds exothermically to a  
20 temperature that in commercial practice is nearly always well above 50°C, typically above about 55 or 60°C and often above about 70°C. Generally the entire temperature rise is due to the exotherm and the process of the invention is preferably conducted on a polymerisable mixture that has a  
25 concentration such that there will be an exothermic rise of at least 20°C and often at least 30°C and frequently at least 40°C. These exothermic temperature rises, and ultimate temperatures, are very much higher than those encountered in soil stabilisation.

30 Thus in the invention the amidase is incorporated in the polymerisable mixture, generally before any polymerisation occurs, and so is exposed to the presence of a large amount of monomer and to the significant exotherm, and it would have been thought that these two conditions  
35 would have been undesirable. However we have surprisingly found that the presence of the amidase in a typical process can reduce the amount of contaminating monomer from, say,

0.4 to 1% (based on polymer) to much lower and more acceptable levels, for instance 0.1% or less. In particular, it is easily possible to reduce the amount of residual (meth) acrylamide by at least 50%, and often at least 80%, by the process of the invention. The amount of residual monomer can be reduced to below 0.01% by weight based on polymer. Further, the presence of the amidase does not seem to increase unacceptably the anionic content of the polymer. For instance, acrylamide homopolymer is usually contaminated with small amounts of acrylic acid anyway, and the presence of the amidase does not lead to any unacceptable increase in the amount of acrylic acid copolymerised with the acrylamide.

These results are very surprising. It would have been expected that the amidase would have converted a significant amount of acrylamide in the initial polymerisation mixture to acrylic acid and it would have been expected that the exposure to the polymerisation exotherm would have deactivated the amidase. It seems that the presence of the polymerisation mixture renders the amidase less sensitive to the temperatures that exist during polymerisation than it would be if it was exposed to the same temperatures in the absence of the polymerisation mixture.

The polymerisation process can be any conventional process of polymerising water soluble ethylenically unsaturated monomers and can thus be solution, precipitation, reverse phase or bulk gel polymerisation. The process is preferably conducted to produce particulate polymer. This can be a stable dispersion of polymer particles in oil, as made by reverse phase polymerisation to a small particle size, typically below 10 $\mu$ m. Preferably the particles are substantially dry. For instance the reverse phase dispersion of small particles may be subjected to azeotroping in conventional manner to remove most or all of the water.

The preferred products of the invention are, however, powdered products and these may be obtained either by reverse phase bead polymerisation followed by separation and drying of the beads, or by bulk gel polymerisation followed by drying and comminution, all in conventional manner. In general therefore the processes of the invention yield products comprising particles having a size of from  $0.05\mu\text{m}$  to  $1\text{mm}$ , and most preferably produces powder (either beads or comminuted gel) having a particle size of  $100\mu\text{m}$  to  $1\text{mm}$ .

The polymerisation process may be conducted in a conventional polymerisation reaction vessel. In the laboratory this typically may have a size of, for instance, at least 1 litre but in commercial production it will normally have a size above 50 litres, e.g., such that a batch of polymer that is produced will have a dry weight of at least 10kg and usually at least 100kg.

The polymer can be a substantial homopolymer of acrylamide or methacrylamide if the polymerisable mixture consists substantially only of (meth) acrylamide, optionally with a cross linking agent.

Often the polymer is a copolymer of (meth) acrylamide with other ethylenically unsaturated monomer that forms a water soluble blend with the (meth) acrylamide. The amount of comonomer with the (meth) acrylamide, can be up to, for instance, 80% by weight but generally it is not more than 50% by weight and frequently it is not more than 20% by weight.

This other monomer is generally ionic, either anionic or cationic. Typical anionic monomers are ethylenically unsaturated carboxylic monomers such as (meth) acrylic acid and ethylenically unsaturated sulphonic acids, for instance vinyl sulphonate or allyl sulphonate or 2-acrylamido methyl propane sulphonate.

Instead of copolymerising with anionic monomer, it may be copolymerised with cationic or potentially cationic monomer. For instance it may be copolymerised with

dialkylaminoalkyl (meth) -acrylates and acrylamides as free base, acid addition or quaternary ammonium salts. The invention is of particular value when applied to polymers of acrylamide alone or acrylamide with acrylic acid (or  
5 water soluble salt thereof) in an amount that is generally below 60% and often below 40% by weight of the polymerisable mixture.

If it is desired to make a cross linked, water absorbent polymer (e.g., one having a gel capacity of above  
10 50g/g deionised water) then a cross linking system must be incorporated and the product is often a powder. Some or all of the cross linking can be through pendant groups, for instance by ionic cross linking or by internal esterification between hydroxy and carboxylic groups, but  
15 preferably the cross linking agent is a polyethylenically unsaturated monomer, such as methylene bis acrylamide or any of the other materials that are conventionally considered as cross linking agents for acrylamide polymers. The amount of cross linking agent is generally at least  
20 0.01%, typically up to about 1 to 2%.

The polymerisable mixture will be an aqueous solution of the chosen monomer or monomers and will contain conventional polymerisation additives such as initiators. The molecular weight of the final polymer can be controlled  
25 in conventional manner, for instance by appropriate selection of the amount or solubility of initiator.

Although the processes of the invention are exothermic, it is naturally desirable that the temperature should not be too high. Generally the temperature is not  
30 allowed to rise above 105°C and preferably is held below 90°C and usually below 85°C. Preferred temperatures are often in the range 60 to 75°C. The temperature may be controlled in known manner, for instance by reliance on the heat sink properties of the solvent or continuous phase in  
35 precipitation and reverse phase polymerisations, by reliance on appropriate selection of the concentration of the polymerisation mixture and on the bulk of the mixture,



and by cooling or by the inclusion of heat sink materials such as described in EP 0123486.

The invention is of particular value when conducted as a bulk gel polymerisation to a temperature of about 60 to 85°C, preferably about 60 to 70 or 75°C.

Typically the monomer is present as an aqueous solution having a monomer content in the range 20 to 50%, often 25 to 40%, by weight.

Any of the amidases that are known for converting acrylamide to acrylic acid can be used in the process of the invention. Particularly preferred are *Brevibacterium ammoniagenes* especially those described in JP-A-53086078. Preferably the seed strain of *B. ammoniagenes* is cultured at 25-35°C and pH 6.5-8.5 in a liquid culture medium containing carbon source, nitrogen source, inorganic salts and other nutrients. After cultivation the bacterial body is separated by filtration and the crude enzyme can be obtained by drying the bacterial body by acetone or by freeze drying and breaking the bacterial cells by mashing in buffer solution or subjecting to supersonic waves. Preferred species are ATCC 1641, ATCC 6871 and ATCC 6872. Other suitable amidases are those described in JP-A-53086079. These include the intracellular enzyme of *Brevibacterium acetylicum*, *B. helvorum*, *B. leucinophagum*, *B. linens* or *B. vitarumen*. They may be cultured in the similar manner. Preferred materials are *B. acetylicum* ATCC 953, *B. helvolum* ATCC 11822, *B. leucinophagum* ATCC 13809, *B. linens* ATCC 8377 and *B. vitarumen* ATCC 10234.

Other suitable enzymes are derived from mixtures of *Bacillus* and *Pseudomonas*, e.g., *Bacillus sphaericus* IAM 1286 and *Pseudomonas putrefaciens* ATCC 8071 or from mixtures of *Brevibacterium* (except for *B. ammoniagenes*) and *Pseudomonas* e.g., *B. acetylicum* ATCC 953 and *P. putrefaciens* ATCC 8071 or mixtures of *Brevibacterium* and *Bacillus*, e.g. *Bacillus brevis* IAM 1031 and *Brevibacterium ammoniagenes* IAM 1641, as described in, respectively, JP-A-52099281, JP-A-5294473 and JP-A-52094470.

Certain species of *Rhodococcus*, *Arthrobacter* or *Pseudomonas* e.g. *P. chloraphis*, will also provide amidases suitable for use in the invention.

5 It will be appreciated that the amidase may be pure or semi-pure or may be bacterial cells or any other fraction having the desired enzyme activity for converting acrylamide. Cofactors and other materials that promote enzymatic activity may be included in the aqueous gel with the enzyme.

10 The process is of particular value when the polymerisable mixture and the polymerising conditions are such that, in the absence of the amidase, the free monomer content of (meth) acrylamide in the final polymer is in the range 0.4 to 2%, generally 0.5 to 1%. The inclusion of  
15 the amidase results in the actual free monomer content always being less than the content obtained in otherwise identical process conditions, typically being less than half of the free monomer content that would exist in the absence of the amidase. Typically this amount is not more  
20 than 50, and often not more than 30 or 15, percent of the amount in the absence of amidase. For instance the amount can easily be below 0.1%, often below 0.005%.

#### Examples 1-7

25 An aqueous solution (100 parts) comprising acrylamide (21 parts) and sodium acrylate (9 parts) at pH 7 was chilled to 0°C and deoxygenated by passage of a stream of nitrogen for 15 min. An aqueous suspension containing amidase enzyme at 53 units/ml (1.9 parts) was then added to the monomer mixture.

30 Polymerisation of the unsaturated monomers was initiated by addition of 1% aqueous ammonium persulphate (APS) (0.5 parts) and 0.35% ferrous ammonium sulphate (FAS) (0.2 parts). After 50 mins. the mixture had set to a gel and had reached 63°C.

35 A control polymerisation (Example 1C) was carried out simultaneously with the same mixture but omitting the amidase solution.

The two hot gels were left to stand for 2h and cut into strands with a mincing machine and further broken down into gel chips. These were left to stand at 20°C for 16h and dried in a fluid bed dryer at 80°C for approximately 30 mins.

Both the test and control products were analysed for residual acrylamide monomer content by the method described in the booklet "Determination of Acrylamide Monomer in Waters and Polymers 1987" published by Her Majesty's Stationary Office, P.O.Box 276, London. The process was repeated at various amidase contents and at various initiator concentrations and the results are set out in the following table. Examples 1C, 5C, 6C and 7C are comparative examples conducted in the absence of amidase.

Example	APS	FAS	Amidase	Acrylamide
1C	0.5	0.2	0	0.24%
1	0.5	0.2	1.9	0.03%
2	0.5	0.2	0.5	0.10%
3	0.5	0.2	1.0	0.05%
4	0.5	0.2	3.0	<0.01%
5C	0.4	0.15	0	0.35%
5	0.4	0.15	1.9	0.06%
6C	0.75	0.3	0	0.12%
6	0.75	0.3	1.9	0.01%
7C	1.0	0.4	0	0.06%
7	1.0	0.4	1.9	<0.01%

It is apparent from these results that it is possible in the invention to achieve reductions in acrylamide well above 50%, and frequently above 90%, of the amount of residual acrylamide obtained when the process is conducted without the addition of amidase.

#### Example 8

A similar polymerisation procedure was followed to the method given in Example 1 except that the temperature of the gel reached 70°C. The residual acrylamide content of the dried gel was 0.16% when polymerisation was in the

presence of amidase, and 0.33% when in the absence of amidase.

Example 9

- 5 A similar polymerisation procedure was followed to the method given in Example 1 except that the temperature of the gel reached 76°C. The residual acrylamide content of the dried gel was 0.24% when polymerisation was in the presence of amidase, and 0.36% when in the absence of amidase.

CLAIMS

1. A process for making polymer of (meth) acrylamide comprising providing an aqueous polymerisable mixture containing (meth) acrylamide in a reaction vessel, exothermically polymerising the polymerisable mixture and recovering the resultant polymer from the reaction vessel, characterised in that the residual (meth) acrylamide content of the polymer is reduced by incorporating amidase in the polymerisable mixture.
2. A process according to claim 1 in which the polymerisation mixture undergoes a temperature rise during the polymerisation of at least 30°C.
3. A process according to claim 1 or claim 2 in which the temperature of the polymerisation mixture during the polymerisation rises to from 50 to 85°C.
4. A process according to claim 1 in which the temperature of the polymerisation mixture rises during the polymerisation to from 60 to 75°C.
5. A process according to claim 1 in which the polymerisation is conducted as a bulk gel polymerisation and the polymer is recovered as a powder by comminution and drying of the gel.
6. A process according to claim 1 in which the polymerisable mixture comprises 40 to 100% by weight acrylamide and 60 to 0% by weight acrylic acid or a water soluble salt thereof.
7. A process according to claim 1 in which the exothermic polymerisation is conducted under conditions such that the amount of residual (meth) acrylamide obtained in the absence of the amidase would be below 1% by weight based on polymer and the presence of the amidase reduces the residual (meth) acrylamide content by at least 50% to a value of below 0.1% by weight based on polymer.

# INTERNATIONAL SEARCH REPORT

International Application No. PCT/GB 91/01583

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) <sup>6</sup> According to International Patent Classification (IPC) or to both National Classification and IPC IPC5: C 08 F 6/00, C 08 L 33/26, C 12 N 9/80, C 12 S 13/00																	
<b>II. FIELDS SEARCHED</b> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Minimum Documentation Searched<sup>7</sup></div> <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 20%; border-bottom: 1px solid black;">Classification System</th> <th style="border-bottom: 1px solid black;">Classification Symbols</th> </tr> <tr> <td style="padding: 5px;">IPC5</td> <td style="padding: 5px;">C 08 F; C 08 L; C 12 N; C 12 S</td> </tr> </table> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Documentation Searched other than Minimum Documentation to the extent that such Documents are included in Fields Searched<sup>8</sup></div>			Classification System	Classification Symbols	IPC5	C 08 F; C 08 L; C 12 N; C 12 S											
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<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup></b> <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="width: 10%; padding: 5px;">Category<sup>10</sup></th> <th style="width: 70%; padding: 5px;">Citation of Document,<sup>11</sup> with indication, where appropriate, of the relevant passages<sup>12</sup></th> <th style="width: 20%; padding: 5px;">Relevant to Claim No.<sup>13</sup></th> </tr> </thead> <tbody> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="padding: 5px;">US, A, 4996251 (FARRAR ET AL) 26 February 1991, see the whole document <div style="text-align: center;">--</div></td> <td style="text-align: center; vertical-align: top; padding: 5px;">1-7</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="padding: 5px;">US, A, 4925797 (BYROM ET AL) 15 May 1990, see the whole document <div style="text-align: center;">--</div></td> <td style="text-align: center; vertical-align: top; padding: 5px;">1-7</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="padding: 5px;">EP, A1, 0393916 (IMPERIAL CHEMICAL INDUSTRIES PLC) 24 October 1990, see the whole document <div style="text-align: center;">--</div></td> <td style="text-align: center; vertical-align: top; padding: 5px;">1-7</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="padding: 5px;">EP, A2, 0329325 (ALLIED COLLOIDS LIMITED) 23 August 1989, see the whole document <div style="text-align: center;">--</div></td> <td style="text-align: center; vertical-align: top; padding: 5px;">1-7</td> </tr> </tbody> </table>			Category <sup>10</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>	A	US, A, 4996251 (FARRAR ET AL) 26 February 1991, see the whole document <div style="text-align: center;">--</div>	1-7	A	US, A, 4925797 (BYROM ET AL) 15 May 1990, see the whole document <div style="text-align: center;">--</div>	1-7	A	EP, A1, 0393916 (IMPERIAL CHEMICAL INDUSTRIES PLC) 24 October 1990, see the whole document <div style="text-align: center;">--</div>	1-7	A	EP, A2, 0329325 (ALLIED COLLOIDS LIMITED) 23 August 1989, see the whole document <div style="text-align: center;">--</div>	1-7
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<div style="display: flex; justify-content: space-between;"> <div style="width: 48%;"> <p><b>* Special categories of cited documents:<sup>10</sup></b></p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 48%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&amp;" document member of the same patent family</p> </div> </div>																	
<b>IV. CERTIFICATION</b> <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; padding: 5px;">           Date of the Actual Completion of the International Search  <div style="border: 1px solid black; padding: 2px; display: inline-block;">12th December 1991</div> </td> <td style="width: 50%; padding: 5px;">           Date of Mailing of this International Search Report  <div style="border: 1px solid black; padding: 2px; display: inline-block;">- 9. 01. 92</div> </td> </tr> <tr> <td style="width: 50%; padding: 5px;">           International Searching Authority  <div style="border: 1px solid black; padding: 2px; display: inline-block; text-align: center;">EUROPEAN PATENT OFFICE</div> </td> <td style="width: 50%; padding: 5px;">           Signature of Authorized Officer  <div style="border: 1px solid black; padding: 2px; display: inline-block; text-align: center;">M. PEIS</div> <div style="margin-left: 20px; font-family: cursive;">M. Peis</div> </td> </tr> </table>			Date of the Actual Completion of the International Search <div style="border: 1px solid black; padding: 2px; display: inline-block;">12th December 1991</div>	Date of Mailing of this International Search Report <div style="border: 1px solid black; padding: 2px; display: inline-block;">- 9. 01. 92</div>	International Searching Authority <div style="border: 1px solid black; padding: 2px; display: inline-block; text-align: center;">EUROPEAN PATENT OFFICE</div>	Signature of Authorized Officer <div style="border: 1px solid black; padding: 2px; display: inline-block; text-align: center;">M. PEIS</div> <div style="margin-left: 20px; font-family: cursive;">M. Peis</div>											
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III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
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A	EP, A2, 0329324 (ALLIED COLLOIDS LIMITED) 23 August 1989, see the whole document  --	1-7
A	US, A, 4687807 (WETEGROVE ET AL) 18 August 1987, see the whole document  --  -----  --	1-7

**ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO. PCT/GB 91/01583**

SA 51332

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.  
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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